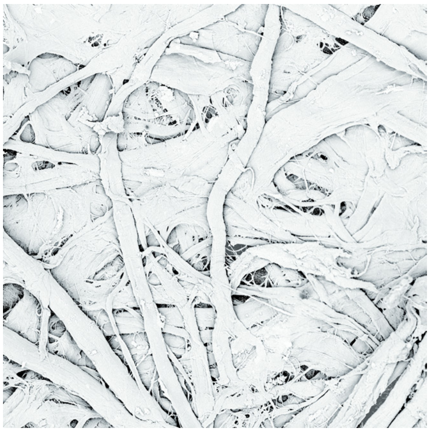
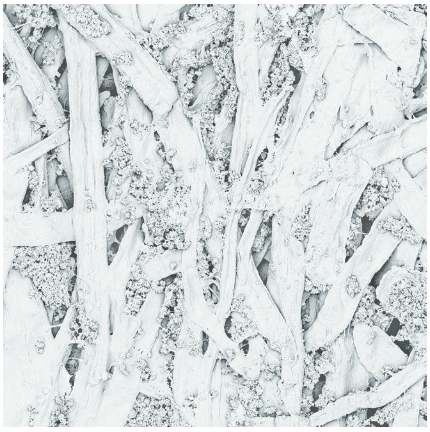


Rag paper from 1665, 1000X



Copy paper with kaolin line, 1000X

Pure paper with polymer line, 1000X

Win Labuda, Christian Wendt

Paper of increased surface purity

for use in clean rooms

Clear & Clean Research Lab,
Revised Issue 1-2020

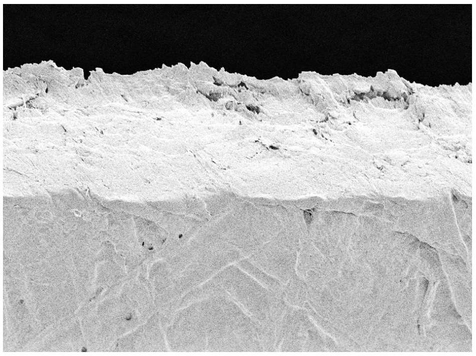


Fig. 1 Cut edge paper manufacturer 1, 300 times (highest edge quality)

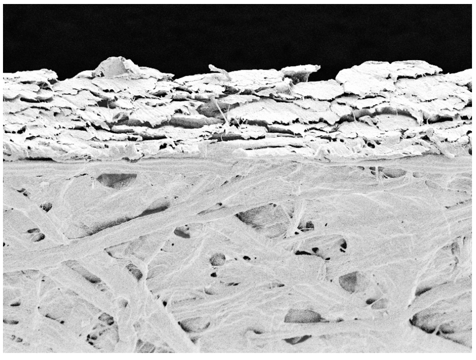


Fig. 2 Cutting edge paper manufacturer 2, 300 times, (medium edge quality)

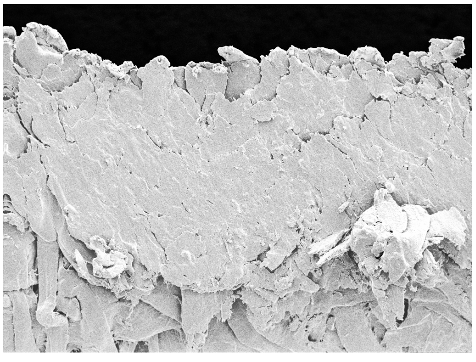


Fig. 3 Cut edge paper manufacturer 3, 300 times (Edge crushed)

In cleanroom operation, as in other hi-tech manufacturing plants, there is a lively exchange of information. Information to employees, equipment manuals, personal notes, sketches and often batch companion logs for the manufactured products – all this information is recorded and distributed internally as well as externally on one of the most mobile data carriers in the world – paper. Even though the digitization of the exchange of information is progressing, paper is still ubiquitous in the cleanroom. Another field of application of pure papers is the separation of such products, which must not lie on a surface before, during or after production, such as silicon wafers. Here, the pure paper is often used as a separator sheet to protect critical product surfaces and to attenuate mechanical shocks during transport.

There are two types of cleanroom papers: some are made of cellulose and have a distinct paper character. The others are made of plastic and are not, strictly speaking, papers. However, for economic and ecological reasons, they were not able to assert themselves quite well in the market. In addition, they cannot be processed there because of the high-temperature fixed rommels in the laser printer. The present essay therefore concerns only cellulosic papers.

Pure papers for documentation are again used in two forms: as a loose sheet stack for the printer or copier operation or in bound form as cleanroom notebooks. Such notebooks must be of a purity-friendly nature: when the lids or individual pages are opened, as few particles as possible should be released. For this reason, such books often have a spiral binding made of plastic wire. The lids are made of clean plastic with rounded corners. The insides are made of checkered printed cleanroom paper. Such notebooks are available in various sizes from A7 to A4. They are used for handwritten recordings in the cleanroom and, of course, for the production of hand sketches.

There is also a requirement profile and a performance profile for pure papers. The requirements profile arises from the need for environmental cleanliness in the processes of pure working. The performance profile, in turn, is based on the technical possibilities of five-stagepaper production. These are:

- Stock preparation (grinding, colouring)
- Leaf formation and surface smoothing
- Equipment with polymer line
- Formatting
- Decontamination

In essence, today (April 2020) the premium class of marketable cleanroom papers largely has an identity between requirements and performance profiles. With papers of this class, the

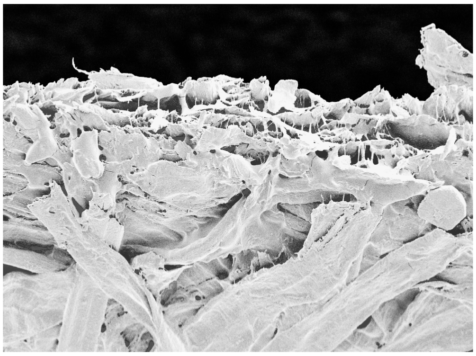


Fig. 4 Cut edge paper manufacturer 4, 300 times (insufficient edge quality)

user has little to wish for. However, some of the papers offered worldwide are not at the top of the quality scale of all technical features and so quality-conscious cleanroom engineers are required to make a requirement-compliant selection.

Of course, papers used in a pure working environment must be of particular nature. Not only should they have a high surface purity in the delivery state, but they may also lose only small amounts of particles, fiber fragments and volatile components into the environment during and after their use in the clean room. In addition, they must have other quality characteristics that are not required for standard papers.

The main features are summarised below:

- high surface purity
- high edge purity
- mäßige triboelectric chargeability
- low ion stock
- sufficient tear resistance and
- low gap inclination

Cleanroom paper production

Before starting production of cleanroom papers, the papermaker must first determine the type of fibres to be used and the grinding degree of them. Production aids of normal paper production, such as kaolin additives as fillers, are excreted for this product. This also applies, if possible, to all bleaching processes and additives that have ionogenic properties. Cleanroom papers are manufactured in the first production step in rolls of about 4 meters wide and 2.5 m in diameter. For better handling, these roles are initially divided into, for example, three smaller roles. In a single production batch, approximately 80 to 100 t of cleanroom raw paper is produced, but its properties are already designed for later use as cleanroom paper. In a further operation, the paper is painted in roll form with a specially formulated, low-ion and particle coating. Manufacturers of pure papers use elastomers, which are used to coat pure papers from both sides as part of their manufacture. These are often carefully selected polymer compounds adapted to this particularapplication. The coating is carried out in order to bind the particles naturally present on the paper surface. A large part of the pores of the paper is closed. On the other hand, this equipment, which is conducive to the purity of use of the papers, creates problems by increasing its triboelectric chargeability, which is automatically coined with such a stroke. After drying the batch, the batch is converted from the roller mould to a flat-bed stack. In another, the most critical conversion process, format papers are now cut from these flat slays in the utility dimensions DIN-A4 or DIN-A5 or others. This process essentially determines the surface purity of the cutting edges of such format papers. For high-quality paper for pure technology, special format cutting techniques are used to

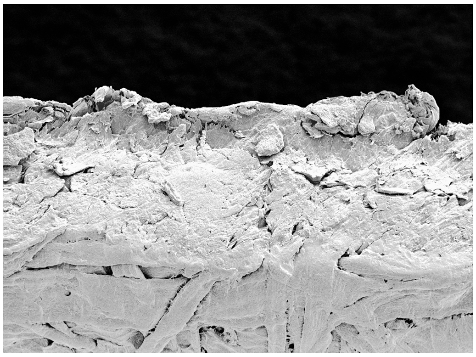


Fig. 5 Cutting edge paper manufacturer 5, 300 times, (medium edge quality)

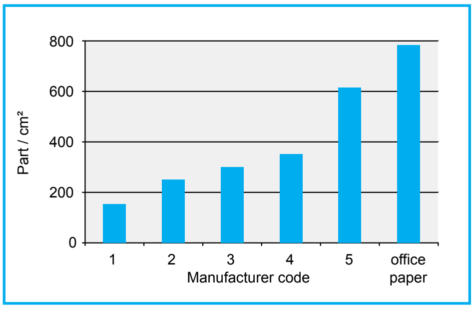


Fig. 6 Comparison of the particle release from clean room papers and standard office paper (5 different manufacturers plus office paper), dipping method

Pure technical testing methods

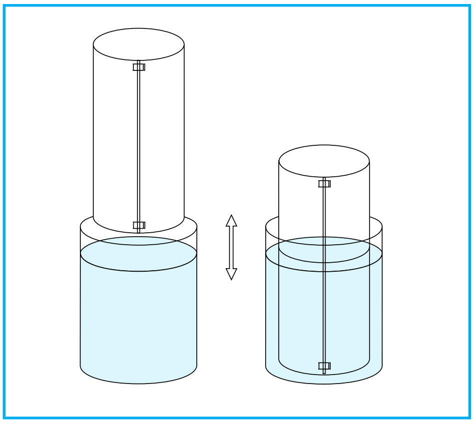


Fig. 7 Scheme: Immersion of a shaped paper in a test liquid (DI water)

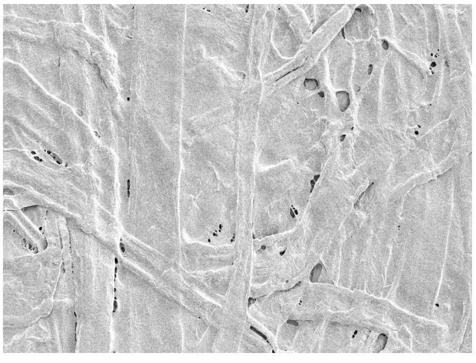


Fig. 8 Surface paper manufacturer 1, 250 times

keep the amount of particle and fiber fragments at the cutting edges of the paper stacks low. The ready-to-sell paper stacks have a height of about 6 cm for 500 sheets of 100 g-paper. In the DIN-A4 format, this corresponds to a critical, particle-laden area of 600 cm2 per sheet. The amount of partial residual contamination in the edge area varies with the cutting method used. Depending on the method the particle-amount on these side surfaces differs in a ratio of about 1:5 between high-quality and less pure papers. Because of the very small market from a paper point of view, there are only five well-known manufacturers worldwide for pure papers. The surfaces and edges of the papers were photographed by electron microscopy. The illustrations were made in our research laboratory (Figs. 1 to 5 and 8 to 12, © Yuko Labuda).

Pure papers are among the large-scale products that constantly pass through the cleanroom - just like overalls, packaging foils, cleaning cloths and mops. Therefore, the cleanroom engineer should pay due attention to this product in his clean-concept. This includes knowledge of the quality characteristics and load limits of such papers.

One of the main requirements for pure paper is its reduced particle release during use. Three ways to make pure paper a particle source:

- due to the nature of the surface
- due to the nature of the edges
- due to the release of low-grade toner particles after printing processes in the copier

This leads to the need to measure the surface purity of the papers. In this context, an American test method (IEST-RP-CC-004) is occasionally referred to, which is often also used for the purely technical qualification of cleanroom cleaning cloths. The test specimen is immersed in a DI water bath and shaken (biaxial shake test). Alternatively, the method provides for the careful casting of the specimen with DI water and the subsequent detection of the particle count in the DI water. The particles released during pouring into the DI water are filtered and the filters are evaluated microscopically. In the past, we had dipped the test specimens three times in our laboratory tests and then drained them. However, this resulted in coefficients of variation above the 40% mark. After reducing the number of dives from three to one, the pegelten coefficients of variation were reduced between 5.6% and 31.3%. In the measurements, which were carried out in our laboratory according to this method, the diving and drip times had to be adhered to very precisely. Otherwise, unacceptable inaccuracies arose, Fig. 6. In summary, we are not really satisfied with this test method, but due to the generally reduced demand for pure papers as a result of digitization measures, we have not been motivated to invest in an improvement of the test methods.

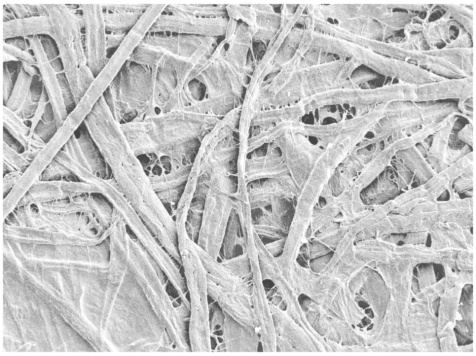


Fig. 8 Surface paper manufacturer 2, 250 times

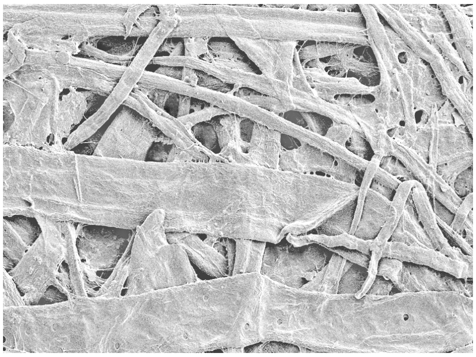


Fig. 10 Surface paper manufacturer 3, 250 times

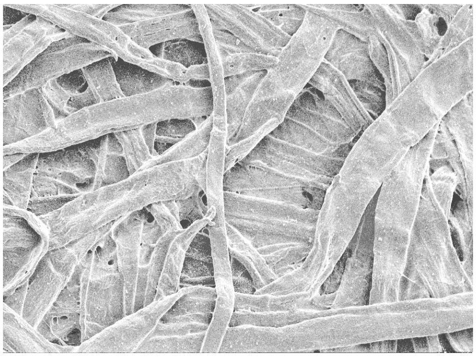


Fig. 11 Surface paper manufacturer 4, 250 times

The cleanroom user is rarely able to check the purely technical quality of cleanroom papers in the delivery state without much effort. For this purpose, it usually lacks the special tools, but also the personnel trained in this direction and the data base for a comparative assessment. For this reason, it makes sense for the user to maintain cooperation with a manufacturer of pure papers or a pure technology laboratory, which, due to its in-house analysis, is also able and willing to provide quality certificates and, if desired, issue a „Certificate of Compliance".

The above-found reliable test method for the number of particles released into DI water during short-term immersion of cleanroom papers unfortunately does not show exactly what the user wants to know as a result. The quality assessment should be based on the quantity of particles replaced when the papers are used and their size distribution. However, there is currently no test method with which the paper handling in the cleanroom is sufficiently and ideally simulated. This is also due to the fact that the particle transfer from the paper to other cleanroom surfaces takes place in two ways:

- *for einen as a contact transfer from the paper surface to any cleanroom surface*
- *and for a change as particle detachment from paper with simultaneous transition into the airborne state with subsequent sedimentation*

The authors have not yet received any results of the study on the percentage distribution of the two contamination routes. The main argument against the above „diving method" remains that the nature of the test specimen changes by diving it into the DI water, while the product does not even come into contact with water in practical use.

Japan reports on the in-house test method of a cleanroom operator, in which an ultrapure wafer with defined contact pressure is pressed onto a sheet of cleanroom paper for a defined period of time. Before and after the test, the number of particles on the wafer is counted and the difference sum is formed. This test initially seems very obvious for simulating thetransfer of particles from cleanroom paper to any surface. On closer inspection, however, the contact transfer is dependent on many parameters with no handling relevance: for example, the electrical charges of the paper as well as the wafer surface,the roughness of the paper surface and last but not least the paper moisture. Provided that all these parameters are controlled, one could investigate whether there are significant correlations between the contact transfer method and the dive method. If this were the case, there would be an interesting possibility of recording by means of contact transfer. In the Clear & Clean research laboratory, a measuring station is ready for contact transfer testing.

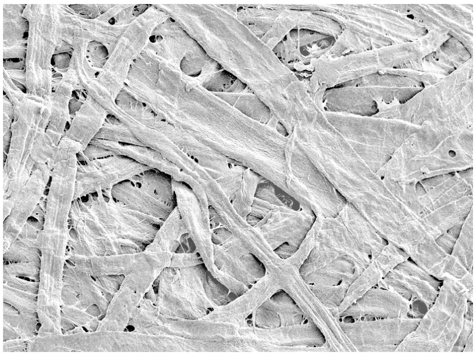


Fig. 12 Surface paper manufacturer 5, 250 times

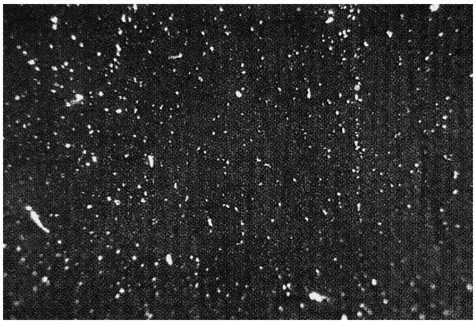


Fig. 13 Microscope image of the cut edge of a paper stack before decontamination

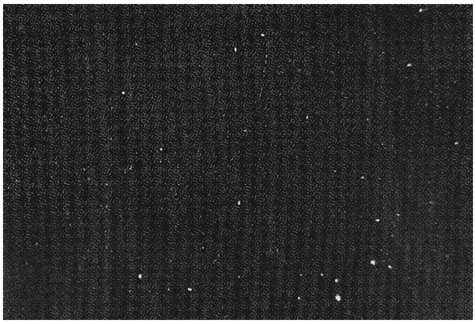


Fig. 14 Microscope image of the cut edge of a paper stack after decontamination

Particles are located on all surfaces of a paper stack, but are much more often at the cutting edges. In the early days of pure technology, there was no introduced method for testing the surface purity of the cutting edges of paper stacks. We therefore had to develop our own method. The result was a mounting device for particles on surfaces (PART-LIFT™-particletransducer). This is a stroke-limited spring stamp with adhesively trained front panel. When pushing this device to the sides of a paper stack, the soluble particles are bound on the adhesive front plate of the transducer. The front panel is of dark coloration and can now be viewed and evaluated under a microscope. The images Fig. 13 and 14 show microscope images of the particle coverings from the cutting edges of a paper stack before and after the cutting edge decontamination. The particle traps manufactured by CleanControlling in Emmingen-Liptingen can also be used for this test. This company also offers an evaluation service.

The particles released by cleanroom papers are not necessarily equivalent in their effect on the process with e.g. polymer particles. This is due to the fact that the material paper always contains a relatively high proportion of sodium ions from its manufacturing process, which pose a danger to the processes of semiconductor production, i.e. wafer production. In this sense, however, released paper particles are also ions that are always released. The better the cleanroom paper, the fewer ions it contains. The measurement of the species contained in the cleanroom paper can be carried out without preparation with the help of energy-dispersive X-ray analysis (EDX). Figures 15 and 16 show corresponding diagrams.

The total amount of ions in the paper sheet can only be determined by extraction. In this method, for example, the paper is immersed in boiling ultrapure water, whereby some of the ions contained therein are released from the paper and transferred into the water. The exact quantity determination of the individual ions in the water bath is then carried out in the Clear & Clean laboratory by means of capillary electrophoresis or ion chromatography. Tab. 1 shows the results of such an extraction.

Cleanroom paper in printer and copier

Cleanroom papers are often printed in office printers or in photocopiers. These are usually designed in such a way that the sheet transport from the paper stack to the printer/copier is carried out by means of a rubberized feed wheel. This means that the paper at the top is always transported. This process results in a strong friction between the conveyed sheet and the underlying paper stack. The triboelectricity produced increases the anti-slip effect between the individual sheets and so paper jam can occasionally occur. In such cases, it is usually assumed that the cleanroom paper is the only cause of the problems encountered.

All images Fig. 1 to 5 and Fig. 8 to 12 were taken with an ISI 60 electron microscope from Akashi-Leitz.

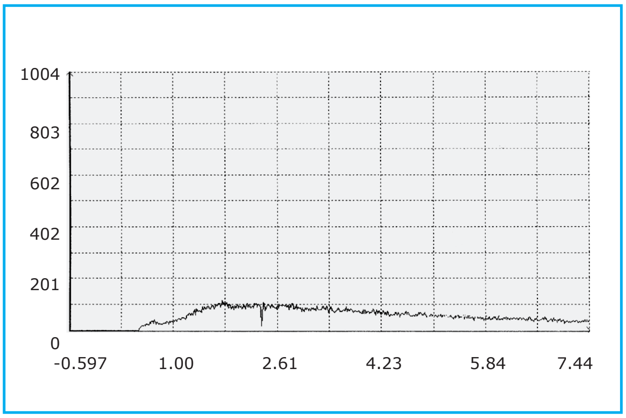


Fig. 15 EDX diagram for cleanroom paper manufacturer 1

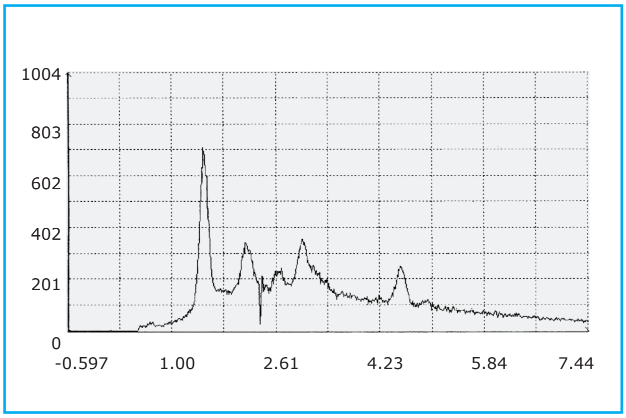


Fig. 16 EDX diagram of cleanroom paper manufacturer 4

The reason for a disturbed paper transport is in principle too high a sliding inhibition between the overlapped leaves. However, there are several possible causes for this:

Experience has shown that the main cause is an unacceptably long open pre-storage of the paper in heated rooms with low relative humidity and associated dehydration of the paper. Dry papers are significantly higher triboelectric rechargeable than moist ones. There are quite inexpensive paper moisture meters, which the large user of cleanroom papers should use to ensure an undisturbed copy operation in the winter months. Other causes include:

- Too high-set contact pressure of the paper feed on the printer/copier
- Too high surface friction between the papers

Anion and cation inventory in ppm Measurement with capillary electrophoresis			
chloride	0.76	ammonium	0.072
nitrate	0.514	Calcium	-
phosphate	0.078	lithium	-
fluoride	0.084	sodium	2.805
nitrite	-	barium	-
sulfate	0.887	potassium	0.103
		magnesium	-
		strontium	-

Tab. 1 Example: Ion inventory of a clean room paper, analyzed by extraction in ultrapure water and subsequent measurement using capillary electrophoresis

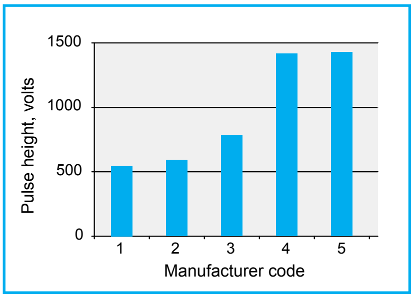


Fig. 17 Test results for the electrical charge pulse height of various clean room papers (measured with a sledge according to Ehrler)

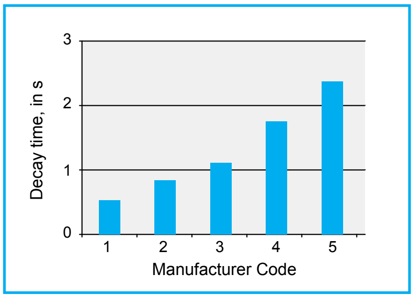


Fig. 18 Test results for the decay time of the charge of various clean room papers (same manufacturer codes as Fig. 16)

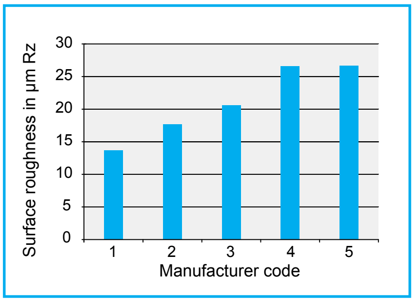


Fig. 19 Surface roughness of the clean room papers from different manufacturers

- Too low derivation of the printer‘s internal corona load of the paper

The triboelectric behavior of the paper is therefore only one of many influencing variables on the parameter sliding inhibition. It is not enough to solve the problem by measuring the electrical surface resistance of the paper when measuring the fault analysis of excessive sliding inhibitions. In most cases, it is the storage and device-specific problems that lead to malfunctions in the paper run.

Triboelectrics can be modified to a large extent by selecting the paper coating. Thus, for the most important cleanroom papers of the international offer, very different charge and discharge diagrams can be found in the test, as can be seen in Figs. 17 and 18 [2].

However, in order to measure the dynamic triboelectricity, a field mill was attached to the inlet shaft of a laser printer in our laboratory and the charge pulse diagrams generated by

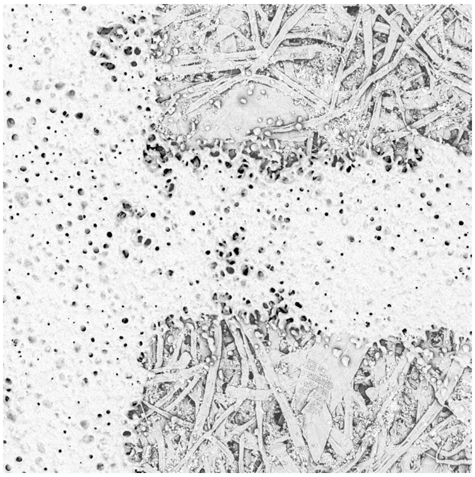


Fig. 20 Toner printing, laser: letter E on kaolin-coated paper

Fig. 21 Toner printing, laser: letter E on pure paper Galaxy®

the paper feed were recorded serially. Fig. 23 shows the pulse series of two differently coated cleanroom papers compared to a standard copy paper from the office industry.

Outgassing at elevated temperatures

In general, paper is considered to be a chemically relatively pure material. However, paper in modern laser printers is temporarily charged by high temperature when fixing the toner particles. Therefore, our laboratory used steam room GC/MS technology to check whether it can be outgassed out of the paper at high temperatures. In this method, a paper test specimen is heated in a closed glass vessel to a temperature of 120 °C or alternatively 170 °C. The resulting outgassing is fed to a gas chromatograph which is coupled with a mass spectrometer (GC/MS). With such an instrument, a chemical analysis up to the ultra-track range is possible. This test showed that no outgassing can be measured at the above-level temperatures. Traces of the polymer line can only be detected by means of special techniques such as the SPME-GC/MC (Solid Phase Micro Extraction), in which the very low outgassings are enriched on an absorber material over a period of one hour and then released again in the GC/MS system for analysis. Such an SPME-GCMS chromatogram of a cleanroom paper shows Fig. 24.

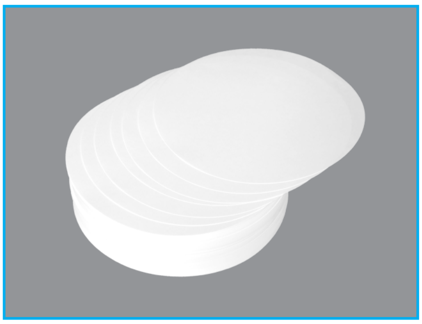


Fig. 22 Separator sheet for the separation of disc-shaped products (wafers, flat glasses, sensors etc.)

The surface smoothness

It can be assumed that smoother paper surfaces release fewer particles during use than rougher ones. This applies in particular to the use as paper in the copier shop, in which a surface friction is work-related. Therefore, the surface of cleanroom paper shouldnot exceed a certain low surface roughness.

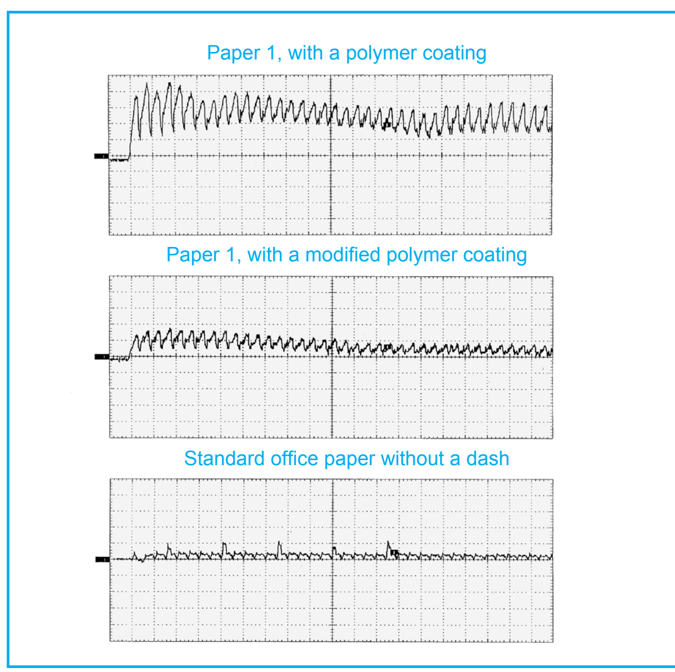


Fig. 23 Triboelectric pulse series (kV) measured on differently equipped clean room papers in printing operation (one pulse per sheet)

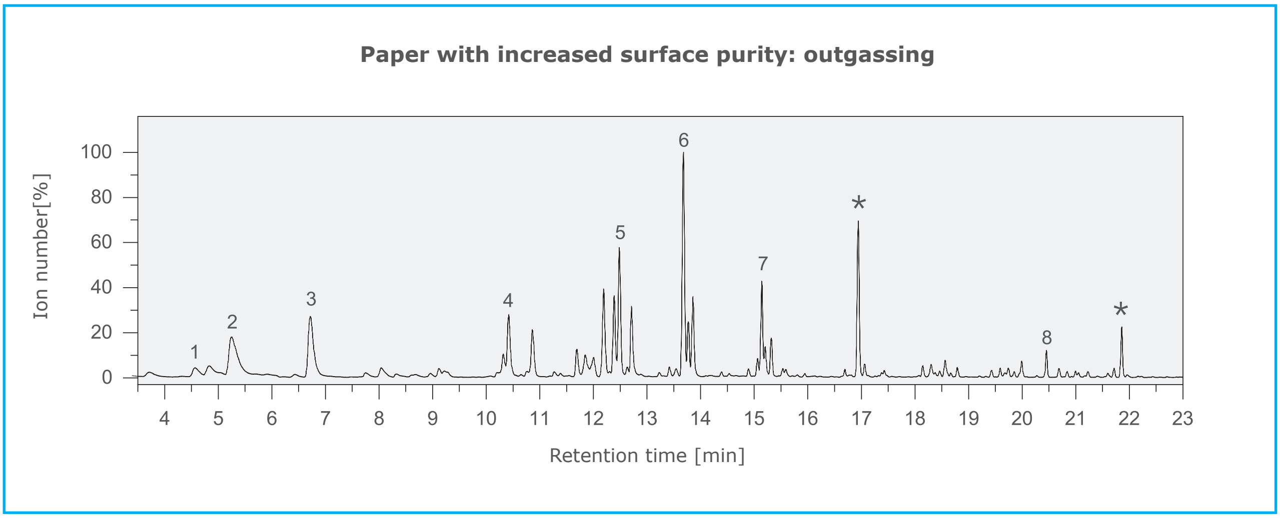


Fig. 24 Chromatogram of an SPME-GC / MS analysis (solid phase micro-extraction), in which the outgassing traces of a clean room paper were accumulated on an absorber material at room temperature over a period of one hour. Without such enrichment, no outgassing can be measured. The substances can be identified by a database comparison of the mass spectra: 1: hexanal, 2: 2,4-dimethylheptane, 3: 2-methyloctane, 4: 2-methyl nonane, 5: tetramethylpentane, 6: undecane, 7: dodecane, 8 : Pentadecan, *: residues of the absorber material. On the one hand, these are odoriferous substances with a natural origin and, on the other hand, they are petroleum extracts, which probably come from the manufacturing process of the polymer coating.

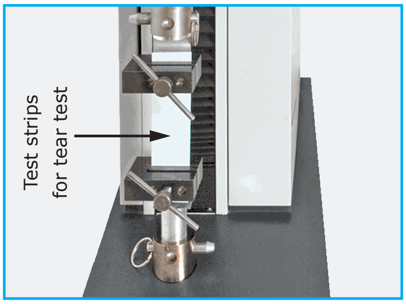


Fig. 25 Maximum tensile force, strain gauge, Adamel

A paper surface of high smoothness is also conducive to a homogeneous print application. The polymeric toner particles are placed on the paper in letter form during printing, melted there and thermally fixed. However, the melting process can only function properly if the temperature of the fixing roller of the printer is set high enough and a sufficient printing of the fuser roller to the paper is ensured. Otherwise, free toner particles remain there, which sooner or later enter the environment and contribute to contamination there. It is therefore advisable to check from time to time the fixing roller temperatures of pure-space-bound copiers. In case of problems with too little toner adhesion on paper, the error must always be searched in this area and not in the paper. Fig. 19 shows a diagram of the surface roughness of marketable papers of pure technology.

The batch differences

Paper is to some extent a living material and so different production batches can be slightly different. While the typical parameters of papers such as thickness, tear-through force and tearing force can be consistently mastered with today's manufacturing technology, one cannot assume that all purely technical parameters show the same values for each production batch. Thus, when painting the papers with a protective layer, the surface roughness may be subject to certain fluctuations. Also, the rolling inclination of papers changes when both sides are coated one after the other with a one-sided coating. In addition, the ionogenic ingredients may be subject to certain fluctuations. The fact that no fillers may be used for smoothing on the manufacturing side of cleanroom papers naturally also causes fiber-dependent differences in surface roughness.

New applications: Organic transistors on paper substrate

Organic transistors for flexible electronic applications are usually applied to polymer substrates. In view of the globally negative effects of plastic waste on the environment on the one hand and on the other hand in terms of the usefulness of certain properties of paper, there has been an increase in efforts in recent years to use paper as substrates for organic transistors. In this sense, the scientists of the Max Planck Institute for Solid State Research Ute Zschieschang and Hagen Klauk have made promising experiments with Galaxy special paper as carrier material. (Clear & Clean GmbH Lübeck) In doing so, they used deposited low molecular weight semiconductor dinaphtol [2,3-b: 2´, 3´-f] [3,2-b-thiophene (DNTT). A thin, high-capacity gate dielectric was used to operate the TFTs at low voltages of 2 V. The TFTs have a charge carrier mobility of 1.6 cm2 / Vs, an on-off current ratio of 106 and a lower threshold slope of 90 mV / decade. In addition, the TFTs have a very large output-difference resistance, which is an important prerequisite for applications in analog circuits and active matrix displays. The research results and applications are described extensively and instructively in the literature. [Lit 3,4].

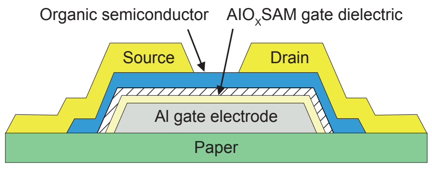


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Fig. 26 Sectional view of a DNTT transistor with a channel length of 40 µm made on Galaxy® clean room paper Clear & Clean GmbH.

In summary, we have fabricated organic transistors direcly on the surface of commercially available paper, without applying a protective or planarization coating. Using the vacuum-deposited small-molecule organic semiconductor DNTT, we have achieved a carrier mobility of 1.6 cm^2/Vs, an on/off current ratio of 10^6, and a subthreshold slope of 90 mV/decade. In addition, the TFTs display a very large differential output resistance.

Authors: U. Zschieschang und H. Klauk

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